

What is claimed is:

1. An article comprising:

5 a metal substrate, having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

10 a catalyst comprising at least one catalyst layer having an outer catalyst layer surface, the catalyst layer supported on the substrate surface; the catalyst comprising at least one catalytically active particulate material, wherein the catalyst layer comprises at least two strata and the outer catalyst layer surface comprises agglomerates of the catalytically active particulate material.

15 2. The article as recited in claim 1 wherein the catalytically active material comprises at least one precious metal component and at least one refractory component.

20 3. The article as recited in claim 2 wherein the catalyst comprises at least two refractory components including a first refractory component and a second refractory component wherein the average particle size of the second refractory oxide component is greater than the average particle size of the first component.

4. The article as recited in claim 1 wherein the agglomerates at the outer catalyst layer surface have an average diameter of from about 20 to about 200 micrometers.

25 5. The article as recited in claim 4 wherein the agglomerates at the outer catalyst layer surface adhere to each other to form peaks from about 20 to about 500 micrometers.

6. An article comprising:

30 a metal substrate having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

a catalyst comprising at least one catalyst layer having a catalyst layer outer surface, the catalyst layer supported on the substrate surface, the catalyst comprising:

- at least one precious metal component;
- 5 at least one first refractory component;
- at least one second refractory component, wherein the average particle size of the second refractory component is greater than the average particle size of the first refractory component.

7. The article as recited in claim 6 wherein the catalyst
10 comprises at least one catalyst layer comprising two regions, a bottom region and a top region, with the bottom region located between the top region and the substrate surface and comprises from 50 to 100 weight percent based on the total of the first and second refractory components of the first refractory component and
15 top region comprises from 50 to 100 weight percent based on the total of the first and second refractory components of the second refractory component.

8. The article as recited in claim 7 wherein the at least one precious metal component comprises
20 at least one first precious metal component in the bottom region; and
at least one second precious metal component in the top region.

9. The article as recited in claim 6 wherein the comprises at
25 least two catalyst layers a bottom layer and a top layer, with the bottom layer located between the top layer and the substrate surface and comprising from 50 to 100 weight percent based on the total of the first and second refractory components of the first refractory component and top layer comprises from 50 to 100 weight
30 percent based on the total of the first and second refractory components of the second refractory component.

10. The article as recited in claim 9 wherein the at least one precious metal component comprises
at least one first precious metal component in the bottom
35 layer; and

at least one second precious metal component in the top layer.

11. The article as recited in claims 6, 7 or 9 further comprising a tie layer comprising a refractory metal compound adjacent to the substrate surface and between the substrate surface and the catalyst.

12. An article comprising:

a metal substrate having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

a tie layer comprising a refractory metal compound adjacent to the substrate surface;

a catalyst comprising at least one catalyst layer having a catalyst layer surface, the catalyst layer supported on the substrate surface with the tie layer being between the substrate surface and the catalyst, the catalyst comprising:

at least one precious metal component and at least one first refractory component, wherein the average particle size of the first refractory component is greater than the average particle size of the refractory metal compound of the tie layer.

13. The article as recited in claims 6, 7 or 10 wherein the catalyst layer comprises at least two strata and the outer catalyst surface comprises agglomerates of the particles of at least one refractory component.

14. The article as recited in claim 13 wherein the agglomerates at the outer catalyst layer surface have an average diameter of from about 20 to about 200 micrometers.

15. The article as recited in claim 14 wherein the agglomerates at the outer catalyst layer surface adhere to each other to form peaks from about 20 to about 500 micrometers.

16. The article as recited in claims 1, 6, 7 or 12 wherein the substrate surface is a rough substrate surface.

17. The article as recited in claims 1, 6, 7 or 12 wherein the metal oxide is alumina.
18. A method comprising the steps of:
- 5 depositing at least two strata of a catalyst on a substrate surface of a substrate to form a catalyst layer, the substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides, and the catalyst comprising at least one catalytically active particulate material.
- 10 19. The method as recited in claim 18 wherein the catalytically active material comprises
- at least one precious metal component; and
- at least one first refractory component.
- 15 20. The method as recited in claim 19 wherein the catalyst comprises at least two refractory components including a first refractory component and a second refractory component wherein the average particle size of the second refractory oxide component is greater than the average particle size of the first component.
- 20 21. The method as recited in claim 18 wherein the step of depositing at least two strata further comprises depositing an aqueous slurry of the catalyst to form each strata as a composition having an amount of fluid to be less than incipient wetness and repeating this step for each succeeding strata.
- 25 22. The method as recited in claim 21 wherein the step of depositing each stratum comprises spraying the slurry.
23. The method as recited in claim 21 further comprising the step of drying each stratum prior to depositing the succeeding stratum.
24. The method as recited in claim 21 wherein each stratum of the layer comprises the same catalyst composition.
- 30 25. The method as recited in claim 21 wherein the strata of the layer comprise different catalyst composition.

26. The method as recited in claim 18 wherein there are at least two catalyst layers.

27. A method comprising the steps of:

forming a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

forming at least one catalyst layer supported on the substrate surface, the catalyst comprising:

at least one precious metal component;
at least one first refractory component;
at least one second refractory component, wherein the average particle size of the second refractory component is greater than the average particle size of the first refractory component.

28. The method as recited in claim 27 wherein the catalyst comprises at least one catalyst layer comprising two regions, a bottom region and a top region, with the bottom region located between the top region and the substrate surface and comprises from 50 to 100 weight percent based on the total of the first and second refractory components of the first refractory component and top region comprises from 50 to 100 weight percent based on the total of the first and second refractory components of the second refractory component.

29. The method as recited in claim 28 wherein the at least one precious metal component comprises

at least one first precious metal component in the bottom region; and
at least one second precious metal component in the top region.

30. The method as recited in claim 29 further comprising the steps of:

forming at least one first slurry comprising the at least one first precious metal component supported on the at least one first refractory component;

forming at least one second slurry comprising the at least one second precious metal component supported on the at least one second refractory component; and

5 mixing said at least one first slurry and said at least one second slurry to make the complete slurry.

31. The method as recited in claim 27 further comprising the step of forming a tie layer comprising a refractory metal compound adjacent to the substrate surface and between the substrate surface and the catalyst.

10 32. The method as recited in claim 27 further comprising the steps of forming at least two catalyst layers a bottom layer and a top layer, with the bottom layer located between the top layer and the substrate surface and comprising from 50 to 100 weight percent based on the total of the first and second refractory
15 components of the first refractory component and top layer comprises from 50 to 100 weight percent based on the total of the first and second refractory components of the second refractory component.

20 33. The method as recited in claim 32 wherein the at least one precious metal component comprises:

at least one first precious metal component in the bottom layer; and

at least one second precious metal component in the top layer.

25 34. The method as recited in claim 33 further comprising the steps of:

fixing the at least one first precious metal component on to the at least one first refractory component; and

30 fixing the at least one second precious metal component on to the at least one second refractory component.

35. The method as recited in claims 27, 28 or 32 further comprising the step of forming a tie layer comprising a refractory metal compound adjacent to the substrate surface and between the substrate surface and the catalyst.

36. A method comprising the steps of:

forming a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

5 forming a tie layer comprising a refractory metal compound adjacent to the substrate surface;

forming at least one catalyst layer supported on the substrate surface, with the tie layer being between the substrate surface and the catalyst layer, the catalyst comprising:

10 at least one precious metal component and at least one first refractory component, wherein the average particle size of the first refractory component is greater than the average particle size of the refractory metal compound of the tie layer.

37. The method as recited in claims 27 or 36 further comprising
15 the step of roughening the substrate surface to form a rough substrate surface.

38. The method as recited in claim 37 further wherein the step of roughening the substrate surface comprises sandblasting the surface.

20 39. The method as recited in claim 37 further wherein the step of roughening the substrate surface comprises chemically treating the surface.

40. The method as recited in claim 27 wherein the substrate comprises a metal alloy containing alumina further comprising the
25 step of calcining the rough substrate surface to form a layer comprising alumina on a substrate surface.

41. The method as recited in claim 40 wherein the step of calcining the substrate is conducted from about 800°C to about 1100°C for from 0.5 hours to about 10.0 hours.

30 42. The method as recited in claims 18 or 36 further comprising the step of calcining the at least one catalyst layer.

43. The method as recited in claim 42 further comprising the steps of forming and then calcining the at least one bottom layer followed by forming and then calcining the at least one top layer.

44. The method as recited in claims 18 or 26 further comprising the step of adding to the catalyst at least one of the following materials to selected from the group consisting of:

- at least one rare earth metal component;
- an oxygen storage composition;
- at least one stabilizer; and
- a compound containing zirconium.

45. A method comprising the steps of:

contacting a gas containing at least one component selected from the group consisting of nitrogen oxide, carbon monoxide and/or hydrocarbon with an article comprising:

a metal substrate, having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and a rare earth metal;

a catalyst comprising at least one catalyst layer having an outer catalyst layer surface, the catalyst layer supported on the substrate surface; the catalyst comprising at least one catalytically active particulate material, wherein the catalyst layer comprises at least two strata and the outer catalyst layer surface comprises agglomerates of the catalytically active particulate material.

46. A method comprising the steps of:

contacting a gas containing at least one component selected from the group consisting of nitrogen oxide, carbon monoxide and/or hydrocarbon with an article comprising:

a metal substrate, the metal comprising iron and aluminum, the substrate having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides:

a catalyst comprising at least one catalyst layer supported on the substrate surface, the catalyst comprising:

- at least one precious metal component;
- at least one first refractory component;

at least one second refractory component, wherein the average particle size of the second refractory component is greater than the average particle size of the first refractory component.

47. A method comprising the steps of:

5 contacting a gas containing at least one component selected from the group consisting of nitrogen oxide, carbon monoxide and/or hydrocarbon with an article comprising:

10 a metal substrate, having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

 a tie layer comprising a refractory metal compound adjacent to the substrate surface;

15 a catalyst comprising at least one catalyst layer having a catalyst layer outer surface, the catalyst layer supported on the substrate surface with the tie layer being between the substrate surface and the catalyst, the catalyst comprising:

20 at least one precious metal component and at least one first refractory component, wherein the average particle size of the first refractory component is greater than the average particle size of the refractory metal compound of the tie layer.

48. The catalyst composition of claims 6, 7, 27, or 36 wherein the average particle size of the second refractory component is at least about one micrometer greater than the average particle size of the first refractory component.

25 49. The catalyst composition of claim 48 wherein the average particle size of the second refractory component is at least about two micrometers greater than the average particle size of the first refractory component.

30 50. The catalyst composition of claims 8, 10, 28, 32 or 33 wherein there is at least one of the first precious metal components and at least one of the second precious metal components, comprises at least one precious metal component not present in the other precious metal component.

35 51. The catalyst composition of claim 50 wherein at least one of the first precious metal components comprises a palladium

component and at least one of the second precious metal components comprises a rhodium component.

52. The catalyst composition as recited in claims 6, 7, 27 or 36 wherein the first and second refractory components are the same or
5 different and are compounds selected from the group consisting of silica, alumina and titania compounds.

53. The catalyst composition as recited in claims 6, 7, 27 or 36 wherein the first and second refractory components are the same or different and are activated compounds selected from the group
10 consisting of alumina, silica, silica-alumina, alumina-silicates, alumina-zirconia, alumina-chromia, and alumina-ceria.

54. The catalyst composition as recited in claim 53 wherein the first and second refractory components are activated alumina.

55. The catalyst composition as recited in claims 1, 6, 7, or 12,
15 further comprising a nickel or iron component.

56. The catalyst composition of claims 1, 6, 7 or 12 further comprises at least one component selected from the group consisting of:

20 at least one rare earth metal component;
 an oxygen storage composition;
 at least one first stabilizer;
 and
 a compound containing zirconium.

57. The catalyst composition as recited in claim 56 wherein at
25 least one of said rare earth metal component is selected from the group consisting of lanthanum components and neodymium components.

58. The catalyst composition as recited in claim 56 wherein the oxygen storage component is selected from the group consisting of cerium and praseodymium compounds.

30 59. The catalyst composition as recited in claim 56 wherein the stabilizer is at least one alkaline earth metal component derived

from a metal selected from the group consisting of magnesium, barium, calcium and strontium.

60. The catalyst composition as recited in claim 56 further comprising a particulate composite of zirconia compound and rare
5 earth oxide.

61. The catalyst composition as recited in claim 60 wherein the rare earth oxide is ceria and, optionally, further comprises lanthana, neodymia and mixtures thereof.

62. The metal substrate as recited in claims 6, 12, 18, 27, 36,
10 45, 46 or 47 in the form of a metal plate at least 0.005 inches thick.

63. The metal substrate as recited in claim 62 wherein the metal plate is at least 0.025 inches thick.

64. The metal substrate as recited in claim 62 wherein the metal
15 plate is corrugated.

65. The metal substrate as recited in claim 62 wherein the metal plate contains a plurality of holes.

66. The metal substrate as recited in claims 6, 12, 18, 27, 36,
20 45, 46 or 47 in the form of at least part of an exhaust system wall defining an exhaust stream passage, wherein the exhaust system wall of exhaust stream passage defines the substrate surface.

67. The metal substrate as recited in claims 6, 12, 18, 27, 36,
25 45, 46 or 47 in the form of a baffle plate of an exhaust system muffler.

68. The metal substrate as recited in claim 67 wherein the baffle plate is at least 0.025 inches thick.

69. The metal substrate as recited in claim 67 wherein the baffle plate is corrugated.

70. The metal substrate as recited in claim 67 wherein the baffle plate contains a plurality of holes.

71. An article comprising:

an engine comprising an exhaust port;

5 an exhaust system connected to the exhaust port, wherein the exhaust system comprises:

a metal substrate, having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

10 a catalyst comprising at least one catalyst layer having an outer catalyst layer surface, the catalyst layer supported on the substrate surface; the catalyst comprising at least one catalytically active particulate material, wherein the catalyst layer comprises at least two strata and the outer catalyst layer
15 surface comprises agglomerates of the catalytically active particulate material.

72. An article comprising:

an engine comprising an exhaust port;

20 an exhaust system connected to the exhaust port, wherein the exhaust system comprises:

a metal substrate, having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

25 a tie layer comprising a refractory metal compound adjacent to the substrate surface;

a catalyst comprising at least one catalyst layer supported on the substrate surface with the tie layer being between the substrate surface and the catalyst, the catalyst comprising:

30 at least one precious metal component and at least one first refractory component, wherein the average particle size of the first refractory component is greater than the average particle size of the refractory metal compound of the tie layer.

73. An article of manufacture comprising:

an engine comprising an exhaust port;

35 an exhaust system connected to the exhaust port, wherein the exhaust system comprises:

a metal substrate, having a substrate surface comprising at least one metal oxide selected from the group consisting of alumina and rare earth metal oxides;

5 a catalyst comprising at least one catalyst layer supported on the substrate surface, the catalyst comprising:

at least one precious metal component;

at least one first refractory component;

10 at least one second refractory component, wherein the average particle size of the second refractory component is greater than the average particle size of the first refractory component.

74. The article as recited in claim 73 further comprising a tie layer comprising a refractory metal compound adjacent to the substrate surface and between the substrate surface and the catalyst.

15 75. The article as recited in claim 71, 72 or 73 as recited in claim 46 wherein the metal substrate is in the form of at least one plate in an exhaust system muffler.

20 76. The metal substrate as recited in claim 75 wherein the exhaust system is configured to direct an exhaust stream to impact with a normal vector component the exhaust baffle plate.

77. The metal substrate as recited in claim 71, 72 or 73 wherein the article of manufacture is selected from the group consisting of a chain saw, a lawn mower, a motor cycle, a generator, a leaf blower, a string mower and a outboard motor boat motor.